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# DSC CALIBRATION FOR THE METHANATION REACTION, CATALYZED BY $Ni/Al_2O_3$ PELLETS

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## ABSTRACT

The nickel catalyzed methanation of CO is followed by DSC. This paper deals with the results, obtained by using $Ni/Al_2O_3$ pellets. Particularly the calibration of the DSC signal and the temperature increase of the pellet, caused by the exothermic methanation reaction, are determined.

## INTRODUCTION

At our laboratory the preparation and the thermal stability of $Ni/Al_2O_3$ catalysts are investigated. These catalysts are to be used for the highly exothermic methanation reaction:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \quad ; \quad \Delta H = -217 \text{ kJ/mole CO} \qquad (1)$$

It was already found, that this reaction could be investigated by DSC very well, using thin layers of catalyst powders (ref. 1,2). Investigation by DSC is also possible with pellets, but the exothermic reaction causes a difference $\delta T$ between the mean reaction temperature $\bar{T}$ and the sensor temperature $T_s$. For the interpretation of the kinetic data it is essential to know this temperature difference.

The thermal conductivity of the pellets is so low, that (particularly in $H_2$) a great part of the evolved heat flows to the gas phase instead of to the sensor. For this reason the DSC signal $\Delta$ cannot be calibrated by melting experiments with indium, but only by direct simultaneous measurement of the reaction rate r (mol/s) by gas chromatography.

## EXPERIMENTAL

The procedure is described in ref. 2. A Du Pont 910 DSC apparatus was used, in the calibrated mode. A pellet is placed directly on the sensor. After reduction (in $H_2$) at 400°C, first a baseline (in pure $H_2$), and then a reaction line (in a mixture of 2% CO and 98% $H_2$) are measured from 100 - 400°C, with a heating rate of 10K/min. The inlet glasflow was kept constant at 2.25 l/hr (NTP). So the maximum conversion ($r_{100}$), that is possible, corresponds with conversion of all CO into $CH_4$: $r_{100} = 5.187.10^{-7}$ mole CO/s.

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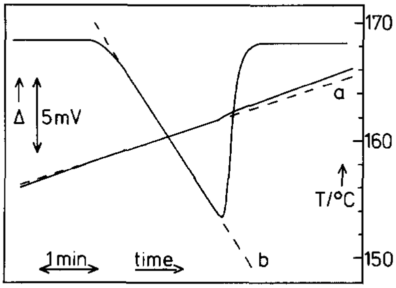

Fig. 1. Melting experiment with indium on the top of a pellet.
a: $T_s$ against time → $dT_s/dt$
b: $\Delta$ against time → $d\Delta/dt$
$\beta_p = (dT_s/dt)/(d\Delta/dt) = dT_s/d\Delta$

In order to obtain calibration constants ($C_{pellet}$), for a number of pellets with different sizes, simultaneously with DSC measurements of the reaction at constant temperature, the conversion of CO has been determined by gas chromatography. The calibration constant is obtained from the equation:
$C_{pellet} \cdot \Delta = Q' = r(-\Delta H)$.

In order to determine $\delta T$, two more experiments (in pure $H_2$) are required. The first one consists of the heating of pellets with indium on top of them. During the melting a linear increase of the sensor temperature with time ($dT_s/dt$) and of the DSC signal $\Delta$ with time ($d\Delta/dt$) is observed. The ratio $\beta_p$ (K/mV) of the slopes $dT_s/dt$ and $d\Delta/dt$ is determined (see Fig. 1). The second extra experiment consists of melting indium directly placed on the sensor. In that case, it is assumed that pratically all heat of melting flows to the sensor and not to the gasphase, resulting in a calibration constant $C_{In}$ (W/mV), according to $Q'_{sensor} = C_{In} \cdot \Delta$. $C_{In} = 2.61.10^{-4}$ W/mV, as measured.

## RESULTS AND DISCUSSION

Figure 2A shows the DSC curves for a powder and a pellet. The pellet shows three kinetic regions. This is clearly shown in the Arrhenius plot (Fig. 2B). *In region I the chemical reaction is rate determining and occurs all over the* pellet. In region III the reaction is limited by diffusion in the gas phase while the reaction only proceeds at the external surface of the pellet. Region II is a transition between pure I and pure III.

### Calibration by gaschromatography

Evaluation of these experiments shows, that in region III the relative conversion $\xi_T$ (= $r/r_{100}$), at standard conditions, is a linear function of the

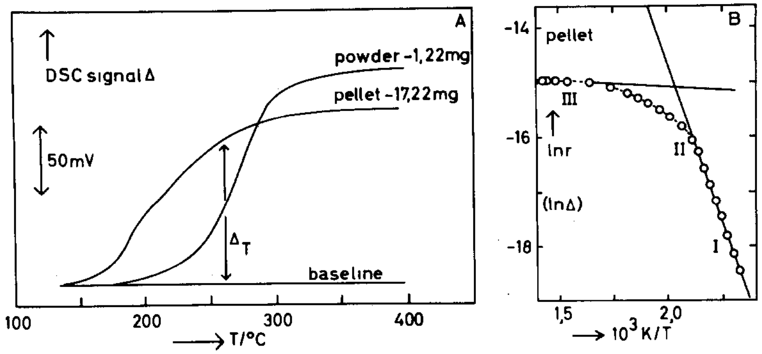

Fig. 2. DSC plot for a pellet and the corresponding powder, prepared by coprecipitation (A); Arrhenius plot for the pellet (B); $\Delta = (-\Delta H)\ r/C_{pellet}$.

external surface area of the pellet $S_p$, that is in contact with the gasphase: $\xi_{395} = 0.613 + 0.00143\ S_p/mm^2$. So $\xi$ varies from 0.64 ($S_p$ = 20 $mm^2$) to 0.72 ($S_p$ = 75 $mm^2$). Some pellets were also analysed at varying temperatures. A straight proportion was found between $\Delta_T$ and $\xi_T$ for every single pellet: $\Delta_T/\Delta_{395} = \xi_T/\xi_{395}$.

This means that the variation with temperature of the calibration constant $C_{pellet}$ is neglectable within our experimental conditions. Thus $C_{pellet}$ can be derived from the DSC plot, provided the dimensions of the pellet are known:

$$Q' = r_{395}\ (-\Delta H) = \xi_{395} \cdot r_{100}\ (-\Delta H) = C_{pellet} \cdot \Delta_{395} \tag{2}$$

TABLE 1

Results for three different catalyst pellets. The calibration constant $C_{pellet}$, temp. increase $\delta T$, relative conversion at 395°C ($\xi_{395}$) and activation energy E for kinetic region I are tabulated.

| Pellet$^x$ | $\beta_p$ | $\xi_{395}$ | $\Delta_{395}$ | $\delta T_1^*$ | $\delta T_2$ | $E_1$ | $E_2$ | $E_3$ | $10^4 \cdot C_{pellet}$ |
|---|---|---|---|---|---|---|---|---|---|
| | K/mV | - | mV | °C | °C | kJ/mol$^o$ | | | W/mV |
| a | 0.26 | 0.65 | 146 | 1.6 | 38 | 108 | 97 | 94 | 5.02 |
| b | 0.34 | 0.68 | 106 | 2.0 | 36 | 111 | 99 | 100 | 7.22 |
| c | 0.06 | 0.67 | 179 | 0.4 | 11 | 94 | 93 | 91 | 4.21 |

a: h = 1.78 mm, d = 2.85 mm; coprecipitate, 70 wt % Ni (ref. 3)
b: h 3.40, d 3.20; deposition precipitate on $\gamma$-$Al_2O_3$, 6 wt % Ni (ref. 4)
c: h 2.90, d 3.60; Ross-Dyson type impregnate on $\alpha$-$Al_2O_3$, 6 wt % Ni (ref. 5)
* $\delta T_1$ calculated for $\Delta$ = 20 mV (region 1), $\delta T_2$ for $\Delta$ at 395°C (region III)
o $E_1$: T not corrected, $E_2$: T corrected, $E_3$: powder

### Determination of δT

The following formulas can be derived by solution of the appropriate heat flow equations:

$$\delta T = f \cdot \beta_p \cdot \Delta \; ; \; \beta_p = C_{In} \cdot h/\lambda \cdot A_s \qquad (3)$$

The value of f depends on the kinetic region: f is about 0.3 for region I (reaction all over the pellet) and f is 1 for region III (reaction only at the surface of the pellet).

The value of $\beta_p$ is inversely proportional with the thermal conductivity $\lambda$ (W/m.K). Once, $\beta_p$ and $\lambda$ have been determined by a single melting experiment, for different pellets of the same kind of catalyst, $\beta_p$ can be calculated by measuring the height h, diameter d and cross section $A_s$ (= $\pi d^2/4$).

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### REFERENCES

1 T. Beecroft, A.W. Miller and J.R.H. Ross, J. Cat., 40 (1975) 281.
2 G. Hakvoort and L.L. van Reijen, Thermal Analysis, Proc. 7th ICTA, Vol. 2, ed. B. Miller, Wiley (1982) 1175.
3 E.C. Kruissink, L.L. van Reijen and J.R.H. Ross, J. Chem. Soc., Far. Trans., 1, 77 (1981) 665.
4 H. Schaper, E.B.M. Doesburg, J.M.C. Quartel and L.L. van Reijen, Preparation of Catalysts III, G. Poncelet et al. eds., Elsevier (1983) 301.
5 K.B. Mok, J.R.H. Ross and R.M. Sambrook, ibid., 291.